CAN WE PREDICT QUANTUM YIELDS USING EXCITED STATE DENSITY FUNCTIONAL THEORY FOR NEW FAMILIES OF FLUORESCENT DYES?

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For a fluorescent dye, the quantum yield characterizes the efficiency of energy transfer from the absorbed light to the emitted fluorescence. In the screening among potential families of dyes, those with higher quantum yields are expected to have more advantages. From the perspective of theoreticians, an efficient prediction of the quantum yield using a universal excited state electronic structure theory is in demand but still challenging. The most representative examples for such excited state theory include time-dependent density functional theory (TDDFT) and restricted open-shell Kohn-Sham (ROKS)[a]. In the present study, we explore the possibility of predicting the quantum yields for conventional and new families of organic dyes using a combination of TDDFT and ROKS. We focus on radiative (k_{r}) and nonradiative (k_{nr}) rates for the decay of the first singlet excited state (S_1) into the ground state (S_0) in accordance with Kasha's rule.[b] For each dye compound, k_{r} is calculated with the S_1-S_0 energy gap and transition dipole moment obtained using ROKS and TDDFT respectively at the relaxed S_1 geometry. Our predicted k_{r} agrees well with the experimental value, so long as the order of energy levels is correctly predicted. Evaluation of k_{nr} is less straightforward as multiple processes are involved. Our study focuses on the S_1-T_1 intersystem crossing (ISC) and the S_1-S_0 internal conversion (IC): we investigate the properties that allow us to model the k_{nr} value using a Marcus-like expression, such as the Stokes shift, the reorganization energy, and the S_1-T_1 and S_1-S_0 energy gaps. Taking these factors into consideration, we compare our results with those obtained using the actual Marcus theory and provide explanation for discrepancy.

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[a] T. Kowalczyk, T. Tsuchimochi, L. Top, P.-T. Chen, and T. Van Voorhis, *J. Chem. Phys.*, **138**, 164101 (2013).

[b] M. Kasha, *Discuss. Faraday Soc.*, **9**, 14 (1950).